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Research on Materials for Advanced Electronic
and Aerospace Application

for the period

July 1, 1974 - June 30, 1975

Under the Direction of

C. D. Armeniades

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T. L. Estle

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and

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I. Introduction

This progress report contains the research reports from the three problem-related areas that have been the subject of the grant during the last three years. We have attempted to improve the coherence of this work by the establishment of a general research objective for each area. The areas and their objectives are:

- A. Optical and Magnetic Memories: The development and understanding of materials most suitable for use in compact magnetic and optical memory systems.
- B. Stress-Corrosion and Hydrogen Interaction with Metals: The suppression of the deterioration of metals by hydrogen.
- C. Polymers and High-Temperature Materials: The improvement of the mechanical properties of polymers with emphasis on low-temperature ductility and compatibility with high-modulus fiber materials.

The report on the research in each area given in Part II is introduced by a discussion of its relation to the general research objective. The work of each investigator is presented under the headings of scientific goals, current objectives and accomplishments. Seventeen investigators from five departments received support for the research described in Part II. Also participating were 18 graduate students (5 foreign) and two postdoctoral fellows. Eleven publications reporting the work during the period are listed in Appendix I. A financial statement covering the period July 1, 1974-June 30, 1975, is given in Appendix II.

Research Reports

A. Optical and Magnetic Data Processing

Staff: H. C. Bourne, Professor of Electrical Engineering
T. L. Estle, Professor of Physics
P. L. Donoho, Professor of Physics
T. A. Rabson, Professor of Electrical Engineering
F. K. Tittel, Professor of Electrical Engineering
W. L. Wilson, Assistant Professor of Electrical Engineering

The goal of this area of research is the understanding and control of those material properties which are important in the functional operation of novel compact non-volatile memory systems, with large storage capability. Of particular emphasis in the Rice program has been the development and study of materials which are used for optical holographic storage in electrooptic crystals, and the manufacture and characterization of amorphous rare-earth transition metal alloys which are useful in magnetic bubble applications.

Two materials which are being studied for possible holographic applications are LiTaO_3 and LiNbO_3 . These crystals are either in a nominally "pure" form, or are doped with various impurities, either while they are grown, or by diffusion after the crystal has been made. Factors such as writing and erasing efficiency, optical quality of the crystal, and fatigue from repeated exposure and erasure have been studied.

The LiTaO_3 crystals are being studied by a group of workers under Dr. T. L. Estle, of the Physics Department, under a project entitled "Optical Data Storage."

1. "Optical Data Storage" (T. L. Estle)

1) Scientific Goals

This project is motivated by the technological goal of high density permanent or re-usable storage of information which could

be rapidly read, written, or erased and which would be inexpensive on a cost per bit basis. Optical storage using volume phase holograms is one of the few attractive possibilities. It is not only promising for storage of digital data for use in serial processing but it has the possibility of being used for analog data and could be an ideal memory for parallel processing. The effects of significant improvement in memory technology would be widespread and the high density feature could be especially important in aerospace applications. The most serious impediment to the development of this approach is the lack of a sufficiently good memory material. Reasonably good characteristics have been obtained for impure electrooptic crystals such as iron-doped lithium niobate (LiNbO_3Fe). However, these materials still require too much energy from the laser to write the holograms. Further progress requires a much better understanding of the complicated solid-state processes whereby the hologram is written or erased. Only then can really good and sensitive optical memory materials be obtained.

The scientific goal of this project is to obtain the required understanding of this photorefractive effect and to thereby answer the following important questions about the material properties:

1. How can one obtain high writing sensitivity?
2. How can one read with low erase sensitivity?
3. How can one deliberately erase with high sensitivity?
4. How can one avoid fatigue, i.e., reduced sensitivity, resulting from repeated write-erase cycles?

All of these questions pertain to sensitivity and this seems to constitute the most important problem. Other potential problems with practical materials will also be investigated.

2) Current Objectives

During the reporting period we anticipated completing measurements of the writing and erasure sensitivity, and other related properties, of manganese (Mn), copper (Cu), and iron (Fe) doped LiNbO_3 and of impure lithium tantalate (LiTaO_3). These data were

to be taken for several wavelengths, polarizations, and intensities of light and for samples treated in various ways and subjected to various external fields. These data were to be compared to optical absorption and electron paramagnetic resonance (EPR) studies of the defects in the crystals. In addition, we planned to dope LiNbO_3 and LiTaO_3 by diffusion to extend the range of dopants available.

Specific milestones were:

1. Obtain data on the sensitivity of impure LiTaO_3 .
2. Identify defects involved in the photorefractive effect in the impure LiTaO_3 .
3. Obtain data on the sensitivity of $\text{LiNbO}_3:\text{Mn}$.
4. Obtain data on the sensitivity of $\text{LiNbO}_3:\text{Cu}$.
5. Obtain data on the sensitivity of $\text{LiNbO}_3:\text{Fe}$.
6. Study properties of diffused $\text{LiNbO}_3:\text{Cu}$.
7. Study properties of 4d and 5d impurities introduced into LiNbO_3 by diffusion.
8. Develop models for the sensitivity data.

3) Accomplishments

The objectives for this reporting period were met in a general sense but the actual research and the results differ in significant ways from those anticipated.

Sensitivity data were obtained on undoped LiTaO_3 which was suspected of being impure. This crystal had been observed to be more than five orders of magnitude more sensitive than nominally pure LiTaO_3 from another source. However, we found that the sensitivity could be changed by 10^5 by oxidation (low sensitivity) and reduction (high sensitivity) and that both samples were comparable (i.e., either pure or with similar effects of residual impurities).

Of the three dopants which make LiNbO_3 rather sensitive, we found that Mn gave the best data, although not the highest sensitivity. The Fe-doped crystals produced very poor quality holographic data because of serious optical scatter which increased with the

integrated optical flux on the sample. The Cu-doped crystals were not as bad as the Fe-doped ones but did show a similar scatter. The absence of any noticeable scatter for Mn-doped LiNbO_3 and a sensitivity within a factor of 10 of that of Fe-doped crystals led us to take data on $\text{LiNbO}_3:\text{Mn}$ to the almost complete exclusion of Cu- and Fe-doped LiNbO_3 . Significant observations on $\text{LiNbO}_3:\text{Mn}$ were usually checked on other materials to determine how general the results were.

The other significant departure from the original objectives was the measurement of different parameters and the use of different techniques than those anticipated. One of those was the study of the photoconductivity of the samples both under uniform illumination and while holograms are being written. Another was the writing of holograms using expanded laser beams so as to cover the entire crystal with the beam.

A large number of observations and conclusions have been obtained, particularly about the charge transport aspects of the process. These are summarized below.

The photocurrent for a homogeneous, uniformly-illuminated sample is nonzero even if no potential is externally applied across the sample. The external-field dependence of the photocurrent allows one to measure the photoconductivity, which is proportional to the intensity, and a parameter having the units of an electric field and which is of the order of 5kV/cm. The sensitivity of the sample upon writing holograms is proportional to the photocurrent. The sample behaves exactly as if photogenerated free carriers drift in a rather large electric field. Since no field need be applied it would have to be an internal field. However this possibility can be excluded since the holographic sensitivity is unchanged if an expanded-beam hologram covering the entire crystal is written with electrodes on the c faces of the crystal shorted. No uniform fields can then exist in the crystal (nonuniform fields would show up as index variations and can also be excluded). It thus appears

that uniform carrier drift occurs with no electric field. This unexpected phenomenon is as yet unexplained but is of major importance in determining the sensitivity of ferroelectric crystals in zero applied field.

Both the electric field parameter (effective drift field) and the photoconductivity are material-dependent parameters. They differ for different dopants and also for oxidized and reduced Mn-doped LiNbO_3 .

Optical erasure sensitivity is probably the second most important material parameter (next to writing sensitivity). We have demonstrated that erasure is a result of drift in the non-uniform hologram field. It cannot occur as a result of uniform drift (which only translates the hologram) and diffusion is usually a slower process in high-sensitivity materials. The erasure time constant can be calculated from the measured photoconductivity of the sample.

During the last year and one half we have observed a fatigue of the writing sensitivity after cyclic writing and optical erasure in all crystals examined. We have now eliminated this fatigue by using an expanded laser beam so as to create the interference pattern throughout the whole crystal. No fatigue occurs if electrodes on opposite c-faces are then shorted. If the electrodes are open or the normal small-beam geometry is used, then fatigue occurs. Although many details still need explanation, it is clear that fatigue results from macroscopic space charge fields which reduce the drift of the charge.

Further proof of this as well as the close relationship between photoconductivity and holographic recording is provided by experiments to simultaneously measure photocurrents while writing holograms. Using the small-beam geometry both photorefractive sensitivity and photocurrent fatigue are quantitatively the same amount.

The study of dopants introduced into LiNbO_3 by diffusion now included V, Fe, Cu, Rh, Pd, Ag, and Pt. The optical absorption spectra and appearance of the Rh and Pd sample suggest that rather uniform impurity concentrations may have been observed but other data are preliminary.

Crystals of LiTaO_3 have also been doped by diffusion. Mn, Fe, and Cu have been successfully introduced. As with LiNbO_3 , iron produces the best sensitivity (for a reduced crystal). Since nominally pure, but reduced, LiTaO_3 is very sensitive, it appears difficult to find dopants which will make it more sensitive. Fe seems to increase the sensitivity by about a factor of 8 and a reduced Cu doped sample has a sensitivity comparable to the reduced pure.

Doping LiTaO_3 results in depoling the crystals. Repoling requires passing a current through them at high temperatures. This seems to influence the sensitivity of many of the samples.

By computer reconstruction we have been able to ascribe some of the unusual dependence of diffraction efficiency upon exposure to the nonuniform intensity profile of the laser beam. In addition computer reconstructions have explained the unusual oscillations in the diffracted beam intensity as a function of angle of incidence in diffused crystals. This results from inhomogeneous impurity concentrations and resultant nonuniform holograms.

A second project involving electrooptic crystals is being directed by Drs. T. A. Rabson and F. K. Tittel of the Electrical Engineering Department.

2. "Optical Data Storage in Ferroelectric Materials" (T. A. Rabson and F. K. Tittel)
- 1) Scientific Goals

The scientific goal for the proposed research is concerned with studying the characteristics of iron doped lithium niobate crystals for suitability in compact real time optical memory and

display systems. Such crystals can be used as optical recording media since they have the property that their refractive index can be changed by the application of light.

The importance of the proposed research to NASA and to scientific technology lies in the need to develop a potentially high density (10^{12} bits/cm²) and fast (gigabits/sec) memory system suitable for both real time and archival computing facilities which can be competitive in size and cost to alternative information storage devices. NASA's Marshall Space Flight Center in Huntsville has already funded a practical real time, page oriented holographic memory program.

In addition, practical, three-dimensional, real time display systems could possibly be developed using these crystals. These systems could be used for air traffic control displays at airports.

2) Current Objectives

The research was directed toward the systematic characterization of the optical and electronic properties associated with the photorefractive mechanism in iron doped lithium niobate crystals. These crystals were selected for study since they appear to be the most sensitive and efficient solid state optical recording medium developed so far.

Detailed measurements of the write-read-erasure properties, in particular diffraction efficiencies of lithium niobate crystals with different iron concentrations and treatment were carried out. Writing efficiencies greater than any reported in the literature have been observed in our laboratory. A specific objective is to unravel details of the photorefractive process in order to make it possible to specify the optimum lithium niobate crystal for efficient optical recording.

Another important goal of this research has been the measurement and optimization of the dynamic characteristics of optical recording crystals with nanosecond and picosecond duration laser pulses with and without the simultaneous application of pulsed

electric fields. In particular, we plan to investigate the apparently improved writing sensitivity using picosecond writing pulses. Workers at Bell Labs have suggested a nonlinear two photon absorption process as the mechanism causing this effect.

3) Accomplishments

1. Writing efficiency, sensitivities for recording and erasure and their dependence on wavelength have been studied for two specially treated Fe:LiNbO_3 crystals.
2. On the basis of the results obtained in (1), a set of 8 Fe:LiNbO_3 crystals with various dopant concentration and treatment have been prepared.
3. Optical absorption spectra at both visible and infrared wavelengths have been obtained for a set of 8 Fe:LiNbO_3 crystals.
4. Read-write-erasure data for some of the crystals have already been collected.
5. Preliminary photocurrent and EPR data in these crystals have been taken. Experiments to obtain information on other properties are underway. These data seem to indicate that the role of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the photorefractive process is not as significant as assumed previously.
6. The experimental system for the pulsed electric field experiment has been built and is being tested.

A second class of materials being studied are amorphous metallic alloys which can be used in magnetic bubble memories. Drs. W. L. Wilson and H. C. Bourne, both of the Electrical Engineering Department are working on this project, entitled "Amorphous Materials for Magnetic Bubble Devices."

3. "Amorphous Materials for Magnetic Bubble Devices" (H. C. Bourne and W. L. Wilson)

1. Scientific Goals

The need for compact, high-capacity non-volatile memories, with no mechanical moving parts is felt in many areas, but

particularly in aerospace applications. Data acquisition, signal processing, and control functions, all require large amounts of storage capacity. The high bit density, zero standby power requirements, and good radiation tolerance of magnetic bubble memories make them attractive choices for these applications. Preliminary reliability figures indicate that all of the advantages of no moving parts are in fact realized with these devices as well.

One of the factors which is limiting bubble memory development at the present time however, is the cost of the garnet material used to support the magnetic bubbles themselves. Sputtered amorphous metallic films of rare earth-transition metal alloys offer one possible solution to this difficulty. Low-cost, plentiful material will be available once these materials are fully developed. The goal of this research is the development of improved amorphous metallic bubble films, and an understanding of the factors which influence their magnetic properties.

2) Current Objectives

We are already able to manufacture thin films of Gd-Co, Gd-Fe and Ho-Co which will support magnetic bubbles. Gd-Co films made from an RF bias sputtering process have been made under a variety of conditions and have been characterized as to their magnetic properties. Most of the parameters which influence these properties have been identified. We are currently working on Gd-Fe, Gd-Fe-Mo, Gd-Co-Mo and Ho-Co films. The first three are made by RF sputtering, the last by thermal evaporation. Objectives for these films include: (a) determine the important parameters which affect the magnetic properties of Gd-Fe and Gd-Fe-Mo films; (b) find the proper mixtures of Gd, Co, and Mo which will result in optimal magnetic bubble material, and then begin a study of wall dynamics in these films; (c) determine the parameters which are most significant in creating the uniaxial anisotropy in the evaporated Ho-Co films.

Further development of our magnetic characterization techniques (e.g., a vibrating sample magnetometer) might also be useful, as this would extend the range of magnetic materials that we could investigate. We also plan to improve the control and development of our RF sputtering system.

3) Accomplishments

The primary aim of this work has been to identify the compositional range over which good bubble characteristics can be obtained. In order to evaluate the magnetic parameters of the films, a number of techniques has been developed. Relative magnetization versus in-plane and out-of-plane drive fields are obtained through either a Kerr rotation optical hysteroograph, or through Hall effect measurements. These data, coupled with bubble statics theory, and the observation of stripe width period using the Kerr effect and an optical microscope, allow the determination of saturation magnetization, and anisotropy field for a large fraction of the samples. An in-plane high-drive field M-H looper allows an independent check on M_s on many of the films. Through these measurements it has been possible to identify those magnetic characteristics which are varied by differing the composition of the materials used in the film manufacture, or by changing the condition under which a given composition is made.

A study was undertaken of the uniformity of the films which were being made, and an effort was made to control those parameters which had the most influence on it. Electric field profiling around the substrate itself appears to be quite significant, as does the uniformity of the target source from which the material is deposited. Electron microprobe studies were made of several films which were over 5 cm on a side, and less than a 1% variation (about the limit of precision of probe) was observed. A study of the temperature of the film during the deposition was also initiated.

Early results with evaporated Ho-Co films indicated many difficulties arising from the inability to obtain good manual control of the two evaporation rates from the e-beam sources, resulting in varying compositions of the films, in a layering manner. Two active feedback control units were designed and constructed which enable much better precision over the deposition parameters of those films. Usable quality bubble material is now being made, and studies of its properties has begun.

B. Stress-Corrosion and Hydrogen Interaction with metals.

Staff: N. G. Alexandropoulos, Visiting Associate Professor of Materials Science

F. R. Brotzen, Professor of Materials Science

C. G. Harkins, Adjunct Assistant Professor of Materials Science

N. F. Lane, Professor of Physics

R. B. McLellan, Professor of Materials Science

J. R. Roberts, Professor of Materials Science

H. E. Rorschach, Professor of Physics

The work of this group has been directed toward the long-range research objective of the establishment of the conditions for the suppression of the deterioration of metals by hydrogen. Stress-corrosion cracking and hydrogen embrittlement occur in many aerospace environments and place structural limitations on the use of a wide variety of high-strength metals and alloys. The deterioration can be inhibited by:

- (a) Limiting the dissociation and absorption of hydrogen at the metal surface.
- (b) Reducing the rate of transport to micro-crack sites.
- (c) Modifying the hydrogen-defect interaction so that crack propagation is retarded.

The research of the staff working in this area is contributing to improved understanding of the mechanisms involved in these three processes.

Professor C. G. Harkins is studying the surface phenomena associated with the dissociation of hydrogen and its entrance into the metal (step (a) above). Step (a) is also the subject of an experimental measurement with X-ray scattering techniques by Professor N. G. Alexandropoulos of the perturbation of the electronic band structure of a metal due to the presence of hydrogen. Band structure effects are important in influencing the solubility of hydrogen. Professor R. B. McLellan's work bears on both steps (a) and (b). He is conducting experimental and theoretical studies of the solubility of hydrogen in alloys (Fe-Ni-H and Fe-C-H), with special emphasis on the trapping of hydrogen by grain boundaries and impurities. Step (b) is also being studied by Professor N. F. Lane, who is making theoretical calculations of the potential energy surfaces for the motion of a hydrogen ion in a metal. These calculations are necessary for the understanding of the kinetics of the diffusion process. Professors J. R. Roberts and H. E. Rorschach are investigating steps (b) and (c) by an experimental study of the hydrogen-lattice and hydrogen-defect interaction. Professor Roberts is measuring the elastic constants and the stress-strain and anelastic damping relations of various hydrogen-containing alloys. Professor Rorschach has developed an electro-chemical method for the direct determination of protonic mobilities in metals. Step (c) is also the subject of the investigations of Professor F. R. Brotzen on models for the accumulation of hydrogen near dislocation arrays and microcracks.

The accomplishment of these projects will lead to improved understanding and control of the entrance of hydrogen into a metal, its transport to microcracks and the consequent enhancement of crack-propagation rates.

1. "Experimental Determination of the Perturbed Valence Band in Metal due to the Presence of Hydrogen" (Nikos G. Alexandropoulos)

- 1) Scientific Goals

The goal of this investigation is to determine experimentally the perturbation of the metal's valence band, due to the presence

of hydrogen, as a function of hydrogen concentration in solid solution.

Through these measurements the behavior of the hydrogen electron in the metal will be investigated in a quantitative way. Such information is necessary to understand the mechanism of hydrogen embrittlement.

The problem of the metal's ductility in the presence of hydrogen is one of great importance to NASA for hydrogen booster containers, and also to ERDA for nuclear fission reactors.

2) Current Objectives

The objective for the current period is to interpret the previously measured data on Nb and NbH_3 . The results will be prepared for publication.

3) Accomplishments

The gamma-ray Compton spectra of Nb and NbH_3 along directions [100], [110], [111] have been measured. The results have been normalized and deconvolved, and the changes in the band anisotropies due to hydrogen have been observed.

2. "Hydrogen Embrittlement of Metallic Materials" (Franz R. Brotzen)

1) Scientific Goals

The deleterious effects of hydrogen contamination on the mechanical properties of most metallic engineering materials are well known. The actual mechanism of this embrittlement, that is, the promotion of crack formation and propagation by hydrogen, is not yet understood, so that it has neither been possible to devise means to eliminate or minimize the hydrogen effects nor to develop economically feasible high-strength alloys that are not subject to this impairment.

The long-range goal of this work is to uncover the physical causes that lead to hydrogen embrittlement and to aim at the development of high-strength materials that are not susceptible to this embrittlement.

2) Current Objectives

It had been the aim to complete the first phase of this project during the six months starting 1 January 1975. This first phase consisted of finding a suitable solution to the diffusion equation for hydrogen moving in a metallic lattice under the influence of a stress gradient created by dislocation arrays or small cracks. This first step in the project assumes a special importance, because it establishes the time dependence of the hydrogen-particle flow (toward the aforementioned imperfections). Based on that knowledge, it becomes possible to correlate experimental results which reflect the time dependence of the embrittling process under constant stress.

The work to be accomplished during the period 1 January - 30 June 1975 was divided into two parts: (a) the calculation of the particle current under the influence of the stress field created by an array of free climbing dislocations or a small pencil crack, and (b) the calculation of the particle current under the influence of the stress field of an edge-dislocation pile-up in equilibrium with an applied sheer stress or a small sheer crack.

3) Accomplishments

The goals set for the research to be performed during the period ending 30 June 1975 were attained. The solution of the diffusion equation in terms of a particle current which crosses a small cylindrical surface whose access coincides either with the lead dislocation of an array of free climbing dislocations or with the tip of a pencil crack, was obtained in closed, approximate form. Similarly, the solution was obtained in terms of the particle flow across the surface of a semi-cylinder which surrounds either the tip of a shear crack or the straight-edge dislocation at the lead of a pile-up in equilibrium with an applied stress. In both cases the assumption was made that the cracks or dislocation arrays are unsaturable. The conditions of the approximation re-

quired that the region for which this calculation was valid would have to be rather small. Furthermore, the approximation limits the results to short initial periods of time.

Two investigations were written up in manuscript form and are presently being reviewed. They will be submitted for publication within a short time.

3. "Hydrogen Embrittlement and Stress Corrosion of Transition Metals" (C. Girvin Harkins)

1) Scientific Goals

Elemental hydrogen and hydrogen compounds comprise the majority of fuels used in aerospace technology such as the space shuttle program as well as in earthbound civilian and military technology. Hydrogen embrittlement and stress corrosion of the metal structures used to store and transport these compounds are major materials compatibility problems. These failure processes are enhanced by the presence of free metal surfaces on which dissociative chemisorption of hydrogen-containing molecules may occur, and are further enhanced by the presence of pre-existing cracks which serve both as stress-concentration sites and as sites for the generation of fresh reactive surfaces as the crack propagation process occurs.

Our laboratory studies of the chemical reactions and the materials failure in hydrogen-containing environments are for both engineering and scientific purposes. The scientific goals include (1) better description of the mechanism and kinetics of hydrogen-containing covalent bond dissociation on transition metal surfaces and (2) better description of how the resulting hydrogen atoms interact structurally and electronically with the metal lattice. Such information suggests methods of impeding failure processes on current materials and characteristics of new materials which may be intrinsically more resistant to failure.

Engineering benefits include (1) extended and improved damage tolerant design parameters and crack rates on structural materials currently used in aerospace applications and (2) additional information on the confidence with which such design data may be used due to limitations in sample design, contamination effects, crack models, pressure ranges, etc.

2) Current Objectives

- (1) Measurement of relative rates of surface recombination reactions versus lattice interaction kinetics.
- (2) Measurement of the relative effectiveness of water vapor and oxygen as inhibitors of the above processes.
- (3) Evaluation of the permeation of thin oxide layers by atomic hydrogen.

3) Accomplishments

Substantial progress has been made in the measurement of crack propagation rates of titanium alloys in hydrogen and deuterium environments, fulfilling the engineering and part of the scientific goals of objective (1). Semi-quantitative studies of the inhibitor processes of objective (2) were also made, and the system was shown to be so sensitive to such contaminants that considerable improvements in the vacuum system were dictated by the results. The mass spectrometer/residual gas analyzer proved to be a significant source of contamination and had to be removed from the system, thereby eliminating measurement of isotopic exchange rates until an alternative is obtained.

The bakeable vacuum system of the last reporting period has been upgraded so that the system background pressure is readily reduced to the order of 10^{-9} torr, with contamination rates the order of 10^{-9} torr-liters/sec and an effective sample lifetime the order of 12 hours. Following consultation with D. P. Williams and H. G. Nelson of NASA-Ames, we converted the crack rate diagnostics from optical readout to electrical readout by installing a load

frame, load cell, and linear differential transformer around the vacuum chamber.

The data collected on uncontaminated samples are not only new information for failure of these alloys in the pressure range of 1-100 torr of hydrogen, but the very large isotope effect observed ($v_{H_2} / v_{D_2} > 2$, where v is the crack-propagation rate) confirms that more than diffusion processes are involved in the rate limiting step. Improved descriptions of the hydrogen embrittlement process must explain this observation and its magnitude.

Substantial progress has also been made toward earlier objectives and current scientific goals concerning electronic interactions of hydrogen with transition metals. We have measured the electrical response of sintered thin films of transition metals. Films of pure titanium, pure iron, and pure palladium have been prepared and characterized both before and after exposure to increasing amounts of hydrogen gas. The data are currently being interpreted on the basis of the pure metal data. This is seen as the basis for experiments on transition metal alloy films closely related to the alloys on which crack rate kinetics are being studied.

4. "Effects of Hydrogen on the Structure of Metals" (Neal F. Lane)

1) Scientific Goals

The scientific goal of this project is to obtain a fundamental understanding, by means of theoretical models, of the manner in which simple defects, such as atomic impurities, migrate in different types of metals. In particular, the diffusion mechanism for atomic hydrogen in metals may be important to the unraveling of the hydrogen embrittlement problem; nevertheless, at the present time it is poorly understood. Extension of our theoretical models to the metal surface can provide important information concerning the adsorption and injection of impurities at the surface. Impurities in alloys can be studied by the same techniques.

2) Current Objectives

The specific objectives of this project for the past year were: (1) refine our theoretical model of H in metals to take into account lattice relaxation, (2) compare theoretical results for diffusion activation energies corresponding to different choices for the diffusion mechanism, (3) initiate ab initio quantum mechanical calculations of H in a Ni crystal.

3) Accomplishments

During the period of this report we have made substantial progress toward all the stated objectives. Some of our results suggest minor shifts in emphasis but overall, our goals remain the same. Progress to date is briefly summarized below:

(1) Refinement of Theoretical Model: In our model, the hydrogen atom is replaced by a proton accompanied by an electron screening cloud, the metal ions are represented by unscreened pseudopotentials, a two-body H-metal potential is calculated to first order, and a full H-crystal potential energy surface is formed by superimposing the 2-body potentials on the static, undistorted, lattice. Recently, we have applied Tewary's infinite-lattice Green's function method to calculate the static distortion of the lattice due to relaxation about a fixed H. Then, the H-crystal potential energy surface is recalculated using the distorted lattice. So far, results have been obtained for V, Ta, and Nb.

(2) Activation Energies for Diffusion: So far, we have considered only two simple diffusion mechanisms, "static" and "phonon induced" and have compared the estimated activation energies in each case. In the "static" case, it is assumed that the hydrogen must surmount a static barrier between favored interstitial sites; the activation energy is approximately 1/2 the barrier height. For example, we obtain "static" barriers (between adjacent "t" sites) of 0.20, 0.10, and 0.23 eV for V, Nb, and Ta, respectively with the choice of

screening parameter r_s = 3 a_0 . If r_s = 4.5 a_0 the values are 0.30, 0.19, and 0.37 eV, respectively. In the "phonon induced" mechanism, both the lattice distortion and the hydrogen move. The "lattice barrier" is taken to be the energy required to move the lattice distortion around an H at one site halfway to the lattice distortion about a neighboring site, i.e., the metal ions all occupy intermediate positions between the extreme configurations where the lattice is relaxed about one or the other adjacent t sites. The "lattice barrier" is calculated to be 0.21, 0.30, and 0.25 eV for V, Nb, and Ta, respectively when the screening parameter is r_s = 3 a_0 . The values for r_s = 4.5 a_0 are 0.44, 0.21, and 0.21 eV, respectively. In some cases the two mechanisms do give different suggested activation energies. The lattice barrier calculations are more sensitive to the form of the H-metal potential than are the static barrier calculations. The former depend on the H-metal force, whereas the latter require only the potential energy surfaces.

(3) Ab Initio Study of H in Ni: The complicated programs to handle the matrix elements of the Hamiltonian and the subsequent variational problem are essentially complete. Calculations have been carried out of the energy levels of pure Ni clusters containing up to two layers (14 Ni atoms) for all the relevant symmetry designations (i.e., irreducible representations). In these preliminary calculations the full (self-consistent) crystal potential of Callaway et al. is used, but the variational wave functions are built up on "clusters" of finite spatial extent. In the case of the 6-Ni-atom cluster a "3d band" (number of closely spaced 3d levels) is found about 0.64 a.u. (Hartrees) above the "4s band" with a width of .073 a.u. For the 14-Ni-atom cluster, the "3d band" broadens and moves closer to the "4s band" as expected from the actual infinite-crystal band structure. We are now studying the convergence of these energy roots as the cluster size is increased. Programs have been written to plot the eigenfunctions so that "electron screening" effects can be observed. Within the next few

months we expect to introduce the H into the cluster and study the local changes in charge density and the behavior of "localized roots."

5. "A Study of the Thermodynamic and Kinetic Properties of Hydrogen-Metal Systems and their Relation to the Electronic and Mechanical Properties" (Rex B. McLellan)

1) Scientific Goals

A study is being made of the thermodynamic properties of H-atoms dissolved in metals and alloys. The basic goal of this research is to use the thermodynamic data as a "probe" to investigate the electronic structure of hydrogen-metal systems. At the same time the mobility of H in metals is being studied. These objectives are of great importance in studying problems such as H-embrittlement and stress-corrosion cracking where solubility and mobility of H are important.

2) Current Objectives

During the current year an intensive investigation of the iron-hydrogen system will be completed. This is a basic system, since many of the engineering problems associated with the presence of H in metals occur in ferrous materials. The effects of purity level and grain boundaries are currently being studied with respect to the "trapping" of H in iron. The objectives established in the previous proposal, i.e., an investigation of the Fe-Ni-H and Fe-C-H systems have been successfully completed. The measured energies of solution for both of these systems indicate some support for recent band-structure calculations for H-metal systems. Solvent atom ordering has no effect on the thermodynamic behavior of hydrogen, nor has the ferromagnetic transformation.

3) Accomplishments

The enthalpy and entropy of dissolved H atoms in iron are being measured by an equilibrate-quench-analyze technique. Because

of the enormous mobility of H in solid iron, the H-Fe equilibrium can be studied at low temperatures (< 300°C). At this time polycrystalline iron samples of varying degrees of purity have been studied. In on-going work, the variation with temperature of H-solubility in a series of Fe single crystals is to be studied.

6. "Stress-Corrosion and Hydrogen Interaction with Metals" (John M. Roberts)

1) Scientific Goals

To obtain (1) fundamental information concerning hydrogen's interstitial site occupation and its associated local lattice distortion in bcc transition metals and (2) fundamental information concerning interstitial hydrogen's interaction with kinks on edge and screw dislocations in the bcc transition metals below and just above the flow stress.

This information will contribute significantly to our understanding and knowledge of the thermodynamic properties of hydrogen solution in these metals and the role of hydrogen-dislocation interactions.

2) Current Objectives

The objectives of this work are: (1) by means of precision elastic constant measurements, to measure the effect of interstitially dissolved hydrogen upon the elastic constants of high purity Ta single crystals in the temperature range of 77 to 450°K; (2) to measure simultaneously the microstrain and ultrasonic propagation (attenuation and modulus defect) properties of tungsten and tantalum single crystals of ultra-high purity and also for the same crystals doped with hydrogen. These measurements will characterize the precise shape of the stress-microstrain relation in the preyield region, the asymmetry effects in the microflow stress and the effects of interstitial impurities on both of the latter. The measurements are to be made at various static stress biases between 4.2 and 300°K.

A microstrain study of Ni single crystals deformed into Stage II is to be carried out after large prestrains and at high stress amplitudes (i.e., at tensile stress amplitudes greater than 3 kgms/mm²); (3) to determine the effect of hydrogen upon the temperature and strain-rate sensitivity of the flow stress, the ductile-to-brittle transition temperature and the fracture morphology of the Ta-H system.

3) Accomplishments

(1) During this reporting period Objective (1) previously described has been completed.

The elastic constants of tantalum were measured in the pure state and at several concentrations of hydrogen doping up to 10.3 atomic % hydrogen. The measurements span the temperature range 23 to -127°C and reveal that $C' = \frac{1}{2}(C_{11} - C_{12})$ decreases with the addition of hydrogen, while all the other elastic constants increased. The temperature coefficients of the elastic constants exhibited no appreciable change due to hydrogen addition.

(2) Considerable progress has been made on carrying out Objective (2).

The prestrain, stress amplitude and temperature dependence of the anelastic microstrain decrement in Ni crystals deformed into Stage II has been evaluated. The modulus defect is observed to decrease from about 20% to 10% in the prestrain increment of 0.15 in Stage II. The decrement in the range 0.01 to .07 is almost linearly stress-amplitude dependent and decreases with increasing prestrain in Stage II and with increasing temperature between 77 and 300°K. Subtraction of the decrement versus stress amplitude data determined under a saturating magnetic field (500 Oe) from that observed at zero magnetic field reveals the magneto-mechanical damping to be only 10% of the observed damping, to mildly decrease with stress amplitude and be essentially temperature independent. Consequently, 90% of the microstrain damping appears to be due to dislocation effects. This work is currently being prepared for publication.

(3) Considerable progress has been made in setting up the equipment for carrying out the simultaneous microstrain and ultrasonic attenuation measurements under various stress biases in the temperature range 4.2 to 300°K. Two Ta crystals have been prepared with a resistivity ratio of 2130. One modulus-defect measurement between 77 and 300°K has been made at zero stress bias, and microstrain determinations at 25% of flow stress were carried out which revealed no measurable damping loop.

7. "Proton Transport in Metals" (H. E. Rorschach)

1) Scientific Goals

The immediate goal of this work is to develop experimental techniques to study the hydrogen-lattice and hydrogen-defect interactions that are the rate-controlling factors in hydrogen embrittlement. The mobility of protons in a metal is determined by their interaction with the electrons and with the lattice and its defects. Mobility measurements are thus important for a clear understanding of this part of the embrittlement process.

2) Current Objectives

An electrochemical technique for the direct measurement of the mobility of hydrogen (protons) in metals is being developed. The objectives were:

- A. Formation of liquid junctions with palladium that permit proton exchange.
 - (1) Determination of proton concentrations in metals by electrochemical techniques.
 - (2) Determinations of rate-of-exchange of protons between palladium and an ion-containing solvent.
- B. Measurement of hydrogen mobility in palladium.
 - (1) Injection of protons into palladium from liquid junctions.
 - (2) Demonstration of proton-transport between two junctions.

An additional objective has been to develop a theoretical understanding of the driving force acting on the proton in a metal due to its interaction with the electric field and the electron "wind."

3) Accomplishments

All of the objectives listed above have been accomplished. Protons can be electrochemically injected and removed from palladium by use of a methanol-KCl solution. A palladium wire connecting two solutions can be made to conduct a "protonic" current, if the hydrogen concentration is sufficiently large. This current has been verified in detail through monitoring the build-up with time of protons in one solution and the change in concentration in the metal. A paper on the theory of electrotransport in metals has been submitted for publication. This paper gives a discussion of the magnitude of the so-called "direct" force on an ion in a metal, and shows that the shielding due to the presence of the electrons has the character of a "wind" force.

Work presently in progress is directed toward an improvement of the measuring precision of the protonic current. We intend to try to apply these techniques to the transport of hydrogen in wires of iron and its alloys that contain controlled defects in order to try to understand the hydrogen-defect interaction.

C. Polymeric Systems and High-Temperature Materials

Staff: C. D. Armoniades, Associate Professor of Chemical Engineering

J. L. Margrave, Professor of Chemistry

J. M. Roberts, Professor of Materials Science

R. L. Sass, Professor of Chemistry

L. J. Wilson, Assistant Professor of Chemistry

Research in this area includes four interrelated projects. Three of these are focused on the synthesis and characterization of polymeric systems, which are promising as structural materials for aerospace uses, or possess certain unique properties. The other involves the use of high temperatures, high pressures and other special techniques to develop and study a new lubricant material.

Structural polymers and polymer composites have inherent advantages as materials in space vehicles, because of their high strength-to-weight ratios. Their use is limited, however, by their tendency to degrade at high temperatures ($> 300^{\circ}\text{C}$) and to embrittle at the low temperatures encountered in space. The study of "Structure-Property Relations in Semi-Crystalline Polymers" by Drs. Armeniades and Roberts seeks to understand the molecular origin of low-temperature embrittlement in structural polymers and develop improved compositions and processing methods for these materials. The "Diffraction Studies of Fiber-Resin Composites" by Dr. R. L. Sass utilize laser and X-ray diffraction techniques to investigate polymer-fiber interactions in composites and describe the mechanisms of component adhesion and stress transfer. Both of these projects have resulted in the development of unique laboratory facilities and methodology for the characterization of pure polymers and composites that are being utilized for nondestructive testing of materials of current interest to NASA, through direct interaction with technical personnel in several NASA research centers.

Dr. R. L. Sass, in collaboration with Dr. L. J. Wilson, has synthesized a new metallocopolymeric epoxy system, which may be of considerable value in fiber-resin composites. Current work seeks to improve the homogeneity of the polymers, diversify its composition and synthesis methods and, in collaboration with Dr. Armeniades, investigate its mechanical properties as a function of chemical structure. The possibility of forming magnetically active Iron Chelate Polymers with the unique capacity to show large changes in electrical conductivity or magnetic susceptibility with temperature is also being investigated by Dr. L. J. Wilson.

Another aspect of our development and investigation of "special" polymeric systems is the continuing study of the CFX type fluorocarbon lubricants, developed originally in his laboratories by Dr. J. L. Margrave. These materials are superior to

graphite, molybdenum disulfide and powdered teflon in many applications, because of their high lubricity and excellent thermal stability.

1. "Structure-Property Relations in Polymeric Systems"
(C. D. Armeniades and J. M. Roberts)

- 1) Scientific Goals

(a) to develop instrumentation, capable of measuring low levels of internal friction at temperatures down to 4K, using polymeric specimens in the form of thin films.

(b) To elucidate the role of crystalline defects on the low-temperature internal friction of linear polymers.

(c) To attempt a quantitative correlation between the density of local defects and the corresponding relaxation behavior and low-temperature ductility.

- 2) Current Objectives

Work during this period was focused primarily on two polymers (polychlorotrifluoroethylene and polyethylene terephthalate) which were found to exhibit internal friction peaks around 40K, related to crystal defects. We planned to introduce measurable amounts of crystal defects in specially prepared specimens and obtain quantitative relations between defect density and internal friction behavior. We also planned to measure the low-temperature ductility of these well-characterized specimens in tension and shear.

- 3) Accomplishments

The initial objectives of this research are now largely attained.

(a) We have designed and constructed a high-sensitivity, cryogenic torsion pendulum, capable of measuring internal friction levels down to 10^{-5} in polymer films of 0.2 mm thickness.

(b) It was found that a number of semi-crystalline, linear polymers (polyethylene, polychlorotrifluoroethylene, polyethylene

tetraphthalate and other linear polyesters) show internal friction peaks at temperatures from 25 to 54K (at a frequency of 1 Hertz), which are independent of polymer composition, but are due to localized motions of point defects in the polymer lattice (such as chain kinks).

(c) The intensity of the internal friction peaks bears a direct relation to the density and orientation of these point defects. The activation energy of the relaxation processes is dependent on the overall molecular organization of the polymer.

(d) The correlation of increased internal friction levels with low temperature ductility in structural polymers, (based on postulated mechanical energy dissipation by the molecular motions that give rise to these low-temperature internal friction processes), is tenuous at best. Our microtensile experiments have shown that even small deformations below 77K produce irreversible structural changes, such as crazing and cracking.

It appears, therefore, that the molecular organization (crystalline content, chain orientation) in these polymers may have only a limited role in enhancing low-temperature ductility. While it would be of interest to pursue further the development of theoretical models, relating various types of crystalline defects to internal friction, this course of investigation would start departing from the long-term goals of the IDL effort, i.e., the development of better structural polymers for aerospace applications. Consequently we propose to modify our immediate objectives to stress the role of chemical structure on polymer properties, while continuing to use internal friction measurements as the primary tool for probing structure-property relations. We intend to investigate a number of polyimids of interest to NASA, as polymeric matrices for composite materials, as well as certain unusual epoxy-polyamide-metalorganic complex polymers, synthesized recently at Rice by Drs. Sass and Wilson, which may possess unique physical properties.

2. "Diffraction Studies of Fiber-Resin Composites" (R. L. Sass)

1) Scientific Goals

This project seeks to apply the various techniques of diffraction (Laser light, X-ray) to studies of the structural and mechanical properties of composite materials. Particular attention will be directed to the study of the structural characteristics of the polymer matrix as a function of fiber spacing, temperature and stress. Attainment of these goals is expected to aid in describing the mechanisms of adhesion at the fiber-matrix boundary and of the transfer of stress through the matrix. Such a description would lead to a better understanding of the role of the matrix in determining the ultimate strength of such composites and would aid in formulating composites specific to the needs of NASA and aerospace design.

2) Current Objectives

Because of the highly amorphous nature of the resins used in most composites, the usual diffraction experiments yield little information on the structures of these resins and the changes in structure with temperature and under various stress conditions. The objectives for the current year are: (1) to introduce chemical modifications into a resin polymer which will provide a regular or semiregular array of X-ray scatterers as markers for structural interpretation; (2) to subject these modified polymers to X-ray analysis at different temperatures and widely varying stress conditions in order to correlate microstructural changes with generated stress field; (3) to interpret the X-ray results by laser-diffraction from suitable model systems constructed on a macroscopic scale.

3) Accomplishments

During the past year, efforts have been directed toward preparing heavy atom derivatives of epoxy resins. This work has led to a series of interesting new polymers which may have considerable

value in the formulation of fiber-resin composite materials. Many polymeric systems have been developed with useful properties obtained through cross linking with a variety of polyfunctional organic molecules. We have used, as a new form of cross linking molecule, difunctional ligands which have coordinated transition metal ions. Specifically, Ni(II) salts have been reacted with 4-amino-pyridine (4-AP) to form the ion $\text{Ni}(4\text{-AP})_4^{+2}$. Reaction with Epon-830 at 40-50°C yields a polymeric material which has mechanical properties similar to normal epoxies. Infrared spectra of the complex indicate that the metal coordinates to the ring nitrogen atom of the 4-aminopyridine molecule. Chemical analysis agrees with the formula $\text{Ni}(4\text{-AP})_4^{+2}$, probably in a square planar array. The chloride, bromide and tetrafluoroborate salts of this complex have been cross-linked with Epon resins. The mixtures undergo a color change on curing, resulting in green (tetrafluoroborate), blue (chloride) and brown (bromide) plastics. All are stable in water and in air up to temperatures of at least 250°C. The physical properties of the cured resin are very dependent on exact curing conditions and on the Epon/complex ratio used in formulation. We have experienced some difficulty obtaining complete cure. The inorganic ionic cross linking complex is a solid and is not soluble in Epon. If this solid is suspended in the Epon, the cured material exhibits micro-crystalline inclusions of the unreacted complex when viewed in thin section with the light microscope. Work is in progress to determine more suitable curing conditions by pre-dissolving the complex in methanol before adding it to the Epon. The mix has an indefinite pot life at room temperature. Thus, the methanol can be removed in a procure stage, resulting in a more homogeneous cure mixture. It is anticipated that increasing the homogeneity of the final cure will result in a considerably stronger resin. The presence of ionic centers in this material should lead to increased bonding potential to ionic or polarizable materials such as graphite.

3. "Magnetically Active Iron Chelate Polymers" (L. J. Wilson)

1) Scientific Goals

The goal of this research is to synthesize, characterize, and study certain new metal chelate polymers of iron, whose conductivity properties should be strongly dependent upon externally applied physical stimuli, such as temperature, pressure, and perhaps visible-ultraviolet radiation. To achieve such unique conductivity properties we shall take advantage of the fact that Fe(II), in appropriate octahedral lattice environments, can exhibit a magnetic spin state equilibrium, "switching" between a state of paramagnetism and one of diamagnetism. Temperature, pressure, and electromagnetic radiation may then be used to control and shift the equilibrium as desired. Ideally, these materials could be reversibly and abruptly interconverted between their various conductivity forms, with insulator (diamagnetic state) \leftrightarrow semiconductor (paramagnetic state) interconversion being a realistic expectation. Single materials displaying such order-of-magnitude variation in their conductivities would be unique and should add a new dimension of flexibility in the construction of electronic apparatus which utilizes conducting and insulating materials. An especially useful application for such materials would be in the area of detection or alarm equipment.

2) Current Objectives

(a) Synthesis of the bipyrimidine (bipyr)-bridged Fe(II) chelate polymers (and their lesser polymer units) will continue to be explored.

(b) Using the $[\text{Fe(II)}(\text{bipyr})\text{Fe(II)}]$ dimer unit as a model system, attempts will be made to prepare the mixed-valence $[\text{Fe(II)}(\text{bipyr})\text{Fe(III)}]$ and fully-oxidized $[\text{Fe(III)}(\text{bipyr})\text{Fe(III)}]$ clusters by electrochemical and/or chemical methods.

(c) The magnetic and electronic structure of the Fe-bipyrimidine dimers, trimers, polymers, etc., will be investigated

by variable temperature magnetic susceptibility measurements, and Mössbauer and UV-VIS spectroscopy.

(d) X-ray structure studies may be initiated on particularly interesting or promising systems (in collaboration with Professor Ronald Sass).

3) Accomplishments

The first objective has been accomplished with the recent isolation of the pure-valence Fe(II) dimer unit of the bipyrimidine chelate, which has demonstrated the ability of Bipy to function in the desired tetradentate fashion.

We have also initiated synthetic work with pyrazine in conjunction with Fe(II) centers in efforts to produce "one dimensional" metallocopolymer structures with anisotropic electrical conductivity properties.

Finally, as part of our continuing effort to elucidate spin equilibria for materials design purposes, we have studied via variable temperature magnetic susceptibility and electronic spectroscopy the $^1A \rightleftharpoons ^5T$ process exhibited by two Fe(II) monomers species, $[\text{Fe}(\text{6MePy})_3 \text{tren}]^{2+}$ and $[\text{Fe}(\text{6MePy})_2 (\text{Py}) \text{tren}]^{2+}$. Through these studies, we have been able to establish the best electronic parameters presently available [i.e., Crystal Field Splittings, $\Delta(^1A \text{ state}) = 12,600 \text{ cm}^{-1}$ and $\Delta(^5T \text{ state}) = 11,700 \text{ cm}^{-1}$, and mean 3d electron pairing energy, $\bar{P} = 12,800 \pm 400 \text{ cm}^{-1}$] for characterization of an Fe(II) $^1A \rightleftharpoons ^5T$ spin equilibrium process of the nature to be operative in the metallocopolymers. This work has resulted in a paper which has recently been accepted for publication.

4. "Properties of 'Special' Materials; Characterization Studies at High Temperatures and Pressures (J. L. Margrave)

1) Scientific Goals

This project is concerned with the use of high temperatures, high pressures, and other special techniques for the study of materials under a variety of conditions to help establish their

usefulness in practical applications. Interest is currently focused on a class of lubricant materials, the solid fluorocarbons falling in the composition range C_4F up to $CF_{1.5}$. Many stoichiometries between these extremes have been reported, and over certain ranges there appears to be the possibility of continuous variation in stoichiometrics. These materials are superior to graphite, to molybdenum disulfide, and to powdered Teflon in many applications because of their high thermal stability, resistance to chemical attack and oxidation. In order to establish these properties more quantitatively and also to understand the types of chemical bonding, studies of thermal decomposition, matrix isolation spectra of decomposition products and ESCA spectra of various solids have been undertaken.

In a separate aspect of the research under this project, the electromagnetic levitation technique is being used for the determination of basic thermodynamic properties of liquid metals.

2) Current Objectives

(a) Characterize the lubricant "CFX" at various stoichiometries in terms of its thermal stability in various atmospheres (O_2 , N_2 , F_2 , etc.) and its stability in vacuum.

(b) Investigate the nature of chemical bonding in CFX and the origin of its lubricant properties, chemical inertness, and potential use as battery material in lithium/CFX high energy batteries.

(c) Establish the properties of liquid metals over wide ranges of temperature using a containerless method of handling and heating the metals, i.e., electromagnetic levitation. Among the goals are (i) the study of the platinum group metals (Ru, Rh, Os, Ir, etc.); (ii) tantalum and tungsten; (iii) lower melting elements of practical importance (Mg, Al, Si, Ge, etc.); (iv) selected binary alloys.

3) Accomplishments

(a) Structural Investigation of CFX and Related Materials

A system involving a semi-micro recording balance along with a controlled temperature region in which CFX can be heated has been used for extensive studies of the thermal decomposition of CFX as a function of temperature in vacuum and in various gaseous atmospheres. The rates of decomposition have also been studied as a function of stoichiometry for materials in the range $\text{CF}_{0.55}$, $\text{CF}_{0.9}$, and $\text{CF}_{1.12}$. The results of such studies indicate (1) that CFX decomposes in vacuum starting at about 450C to produce a variety of perfluorosaturated and unsaturated species, but mainly to produce CF_4 , C_2F_6 , C_2F_4 , and C_3F_8 . Smaller amounts of polyperfluorospecies having as many as eight or ten carbon atoms in the backbone have been observed.

Vacuum decomposition is the fastest and the decomposition of substoichiometric materials, i.e., $\text{C}/\text{F} > 1$, is next. Superstoichiometric materials decompose more slowly by large factors, in some cases as much as a factor of ten more slowly. The thermal decomposition rates in vacuum, in oxygen, and in nitrogen are essentially the same, although the vacuum decomposition of CFX is elemental fluorine. In the presence of elemental fluorine at partial pressures as low as a few torr, one observes only slight decomposition of CFX at nearly 800C. Eventually, of course, and especially at higher fluorine pressures CFX will burn in fluorine to produce CF_4 . There is some evidence for the disproportionation type of decomposition in which CF_4 and other fluorocarbons are evolved leaving a residue of elemental carbon. This is not, however, the major mechanism of decomposition and in oxygen or in fluorine, of course, any carbon produced by disproportionation is burned and it disappears from the system either as CO or as CF_4 .

Another sensitive analytical technique which can provide special information of value in clarifying the decomposition mechanisms involves the direct freezing out on a mirror of the

molecules, fragments, and atoms, which are evolved as a material thermally decomposes. CFX samples have been heated to the same temperature ranges, 400-800°C, as used in the thermal balance studies and the vapor decomposition products have been collected on a metal mirror cooled to liquid helium temperatures. From the infrared spectra of these condensed species, one can make unequivocal identification of the decomposition products. This type of work has been used to show that the primary product of decomposition is CF_4 with the next most common material being C_2F_6 and C_3F_8 . C_2F_4 is also produced. A careful search is currently underway for evidence that might indicate CF_2 , the difluorocarbene, or more interestingly CF or C_2F_2 , difluoroacetylene. This latter species especially would be unique and has currently not been well-characterized in the published literature.

A new instrument for "ESCA" (Electron Spectroscopy for Chemical Analysis) has been put into operation and is currently being used for an important study of the carbon and fluorine characteristic spectra produced when CFX samples of various stoichiometries are irradiated with high energy X-rays so that electrons are ejected from the Cls, Fls shells of the two characteristic atoms. The energy analysis of the electrons ejected allows one to identify the types of carbon-carbon and carbon-fluorine bonding which are involved. In particular, one can identify saturated or unsaturated carbons, covalent or ionic CF bonds, and furthermore, try to get some ideas about the site symmetry around the carbon. Such studies are currently underway.

(b) Levitation Studies of Liquid Metals at High Temperatures

No new projects have been completed during the current research period because the funded efforts have been required to set the ESCA machine into operation and carry out the thermo-decomposition studies. The levitation machine is in good operating condition and a new student has been recruited for working with it. He has begun studies of aluminum and magnesium, and will continue these as he proceeds to work with other low melting metals of practical importance such as silicon, germanium, etc.

Appendix I

Publications During the Period of This Report

A. Optical and Magnetic Data Processing

1. "Pulsed Holographic Recording in Ferroelectric Crystals," T. A. Rabson, F. K. Tittel, and R. R. Shah, *J. Opt. Soc. Am.* 64:1394 (1974).
2. "Study of the Dynamic Properties of Mode-Locked Nd³⁺:Glass Laser Radiation," T. A. Rabson, D. M. Kim, and R. R. Shah, *J. Opt. Soc. Am.* 64:1359-1360 (1974).
3. "Effects of DC Bias on the Fabrication of Amorphous GdCo RF Sputtered Films," H. C. Bourne, R. B. Goldfarb, W. L. Wilson, Jr., and R. Zwingman, *IEEE Trans. MAGNETICS MAG* 11, to be published September 1975.

B. Stress-Corrosion and Hydrogen Interaction with Metals

1. "Hydrogen Interactions with Metals," R. B. McLellan and C. G. Harkins, *Journal of Materials Science* 18, 5 (1975).
2. "Activities in Carbon Austenite," R. B. McLellan, *Met. Trans.* 5, 2676 (1974).
3. "Solute Mutual Interactions in Carbon Austenite," R. B. McLellan, *Scripta Met.* 8, 1287 (1975).
4. "Positional Information in Solid Solution Models," D. C. Parris and R. B. McLellan, *J. Appl. Cryst.* 8, 121 (1975).
5. "Variation of the Elastic Properties of Austenite with Carbon Content," W. J. Arnoult and R. B. McLellan, *Acta Met.* 23, 51 (1975).
6. "H-H-Interactions in the Group V Metals," R. B. McLellan, *Scripta Met.* 9, 681 (1975).

C. Polymeric Systems and High-Temperature Materials

1. "X-Ray Powder Diffraction Study of Poly(Carbon Monofluoride), CF_{1.12}," V. K. Mahajan, R. B. Badachhape, and J. L. Margrave, *Inorg. Nucl. Chem. Letters* 10, 1102 (1974).
2. "An Electronic Structural Study of Some Fe(II) Magnetic Isomers in Solution and a Spectral-Structural Correlation with Their Ni(II) Analogs," L. J. Wilson, D. Georges, and M. A. Hoselton, *Inorganic Chemistry* 14, 0000 (1975) (accepted for publication in November 1975 issue).

Appendix II - Financial Report

NASA Grant NSL 44-006-001

Report of ExpendituresFor the Period

7/1/74 12/31/74

For the Period

5/1/59 12/31/74

Salaries:

Professional	\$26,434.16	\$1,183,213.76
Students	<u>19,940.42</u>	<u>575,089.19</u>
	\$46,374.58	\$1,763,302.95

P/R Benefits: 4,149.13 4,149.13

4,149.13

Indirect Costs:

@50% of salaries in the first \$150,000 expended	\$ 235,429.10
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@25% of Direct Costs not to exceed \$120,000 of the next \$600,000 expended	120,000.00
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@20% of Direct Costs not to exceed \$216,666.67 of the next \$1,300,000 expended	216,666.67
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@55.6% of Salaries through 6/30/73	136,415.29
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@61.5% of 1973-74 salaries	60,624.05
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@53.1% of salaries	<u>\$24,624.90</u>	<u>24,624.90</u>
	\$24,624.90	\$ 793,760.01

Expendables

Supplies & Materials	\$33,359.55	\$ 746,020.02
Minor Equipt.	<u>1,620.07</u>	<u>217,191.69</u>
	34,979.60	963,211.71

<u>Major Equipment</u>	<u>\$ 3,477.02</u>	<u>3,477.02</u>	<u>\$ 421,943.26</u>	421,943.26
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Commitments Outst'g.:

Supplies & Mater.	6,143.93
Minor Equipment	<u>970.00</u>

	7,113.93	7,113.93
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Totals:

	<u>120,719.16</u>
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	<u>3,953,480.99</u>
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Appendix II - Financial Report

NASA Grant NSL 44-006-001

Report of Expenditures

	For the Period		For the Period	
	1/1/75	6/30/75	5/1/59	6/30/75
<u>Salaries:</u>				
Professional	\$30,921.52		\$1,219,135.28	
Students	<u>21,600.39</u>		<u>596,689.58</u>	
		\$52,521.91		\$1,815,824.86
<u>P/R Benefits:</u>	<u>5,084.51</u>	5,084.51		9,233.64
<u>Indirect Costs:</u>				
Q50% of salaries in the first \$150,000 expended				\$ 235,429.10
Q25% of Direct Costs not to exceed \$120,000 of the next \$600,000 expended				120,000.00
Q20% of Direct Costs not to exceed \$216,166.67 of the next \$1,300,000 expended				216,666.67
Q55.6% of salaries thru 6/30/73				136,415.29
Q61.5% of 1973-74 salaries				60,624.05
Q53.1% of salaries 7/1/74-6/30/75		27,839.13	<u>52,514.03</u>	821,649.14
<u>Expendables:</u>				
Supplies & Mat.	\$33,677.75		779,697.77	
Minor Equip.	<u>5,350.84</u>		<u>222,542.53</u>	
		39,028.59		1,002,240.30
<u>Major Equipment:</u>			421,943.26	421,943.26
<u>Commitments Outstanding:</u>				
Supplies & Mat.	5,594.44		5,594.44	
Minor Equipment	4,371.86		4,371.86	
Major Equipment	<u>2,800.00</u>		<u>2,800.00</u>	
		\$ 12,766.30		\$ 12,766.30
<u>Totals:</u>		<u>\$137,290.44</u>		<u>\$4,083,657.50</u>